# Electronic Supplementary Information for

## Nano-Phase Separation and Structural Ordering in Silica-Rich Mixed Network Former Glasses

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**Table S1.** Three-fold coordinated boron speciation and NMR parameters as determined from deconvolution of $^{11}B$ MAS NMR spectra. Uncertainties in isotropic chemical shift ($\delta_{CS}$), quadrupolar coupling constant ($C_Q$), quadrupolar asymmetry parameter ($\eta_Q$) and intensity (Int.) are no more than ±0.5 ppm, ±0.1 MHz, ±0.1 and ±2%, respectively. $\eta_Q$ was constrained to these tabulated values to facilitate fitting of the data. $C_Q$ was also constrained to 2.70 MHz for the ring $B^{III}$ resonance.

| Glass ID | ring $B^{III}$ | | | | non-ring $B^{III}$ | | | | $B^{III}$(P NNN) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\delta_{CS}$ (ppm) | $C_Q$ (MHz) | $\eta_Q$ (-) | Int. (%) | $\delta_{CS}$ (ppm) | $C_Q$ (MHz) | $\eta_Q$ (-) | Int. (%) | $\delta_{CS}$ (ppm) | $C_Q$ (MHz) | $\eta_Q$ (-) | Int. (%) |
| **B16** | 17.4 | 2.7 | 0.1 | 4.6 | 13.3 | 2.66 | 0.2 | 44.7 | 11.6 | 2.49 | 0.2 | 23.9 |
| **B22** | 17.5 | 2.7 | 0.1 | 9.5 | 13.5 | 2.67 | 0.2 | 44.6 | 11.7 | 2.48 | 0.2 | 24.6 |
| **B24** | 17.6 | 2.7 | 0.1 | 11.9 | 13.6 | 2.68 | 0.2 | 43.0 | 11.8 | 2.48 | 0.2 | 24.4 |
| **B26** | 17.6 | 2.7 | 0.1 | 14.3 | 13.6 | 2.68 | 0.2 | 43.0 | 11.8 | 2.47 | 0.2 | 23.3 |
| **B28** | 17.6 | 2.7 | 0.1 | 17.0 | 13.7 | 2.69 | 0.2 | 41.6 | 11.8 | 2.48 | 0.2 | 22.8 |
| **B30** | 17.6 | 2.7 | 0.1 | 19.7 | 13.8 | 2.70 | 0.2 | 40.6 | 11.8 | 2.47 | 0.2 | 22.2 |

**Table S2.** Four-fold coordinated boron populations and $\delta_{CS}$ for the two resolved $B^{IV}$ resonances determined from deconvolution of $^{11}B$ MAS NMR spectra in this series of glasses. Uncertainties in $\delta_{CS}$ and Int. are no more than $\pm 0.2$ ppm and $\pm 2\%$, respectively.

| Glass ID | $B^{IV}(4P)$ | | $B^{IV}(P,Si)$ | | Total $N_4$ (%) |
| --- | --- | --- | --- | --- | --- |
| | $\delta_{CS}$ (ppm) | Int. (%) | $\delta_{CS}$ (ppm) | Int. (%) | |
| **B16** | -4.2 | 22.0 | -2.1 | 4.8 | 26.8 |
| **B22** | -4.2 | 16.9 | -2.0 | 4.4 | 21.3 |
| **B24** | -4.2 | 16.4 | -2.0 | 4.2 | 20.6 |
| **B26** | -4.2 | 15.4 | -2.0 | 4.0 | 19.4 |
| **B28** | -4.2 | 14.5 | -2.0 | 4.1 | 18.6 |
| **B30** | -4.3 | 13.7 | -2.0 | 3.8 | 17.5 |

**Table S3.** Site populations and NMR parameters for Al, as determined using DMFit deconvolution of $^{27}$Al MAS NMR data. Uncertainties in $\delta_{CS}$, $C_Q$, and Int. are no more than $\pm 1$ ppm, $\pm 0.2$ MHz, and $\pm 2.5\%$, respectively.

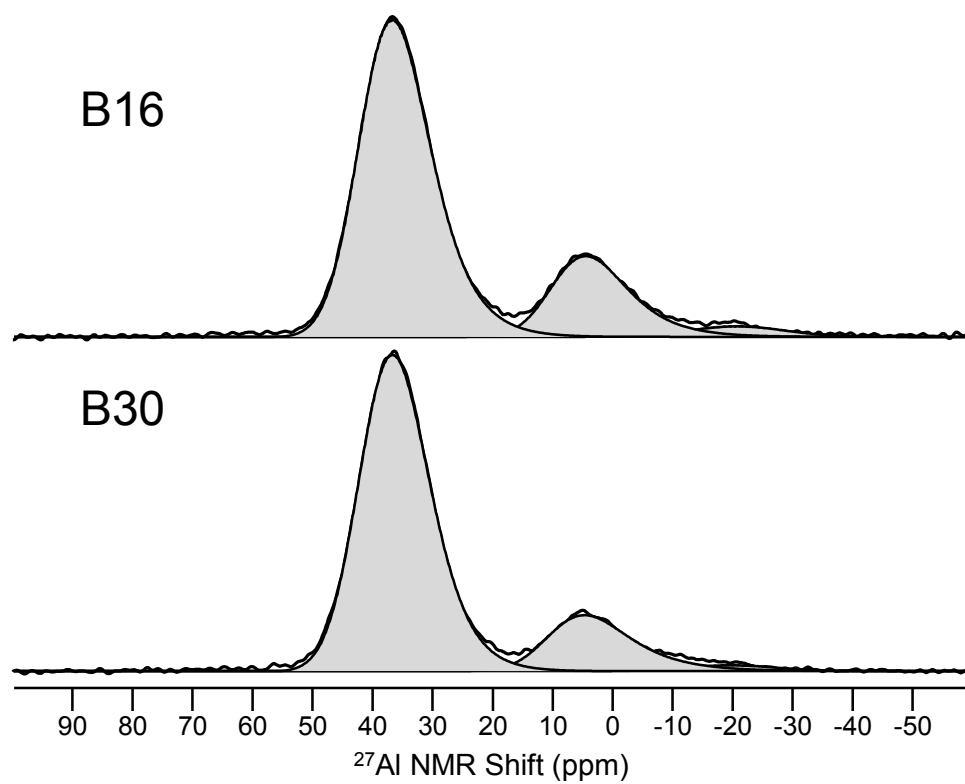| Glass ID | Al$^{IV}$ | | | Al$^{V}$ | | | Al$^{VI}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\delta_{CS}$ (ppm) | $C_Q$ (MHz) | Int. (%) | $\delta_{CS}$ (ppm) | $C_Q$ (MHz) | Int. (%) | $\delta_{CS}$ (ppm) | $C_Q$ (MHz) | Int. (%) |
| **B16** | 41.0 | 5.09 | 76 | 9.4 | 5.61 | 21 | -19.3 | 2.59 | 3 |
| **B22** | 40.8 | 4.88 | 78 | 9.3 | 5.49 | 19 | -19.3 | 2.16 | 3 |
| **B24** | 40.8 | 4.84 | 80 | 9.5 | 5.60 | 18 | -19.3 | 2.12 | 2 |
| **B26** | 40.7 | 4.82 | 81 | 9.5 | 5.60 | 17 | -19.2 | 2.19 | 2 |
| **B28** | 40.7 | 4.78 | 81 | 9.6 | 5.55 | 17 | -18.9 | 2.14 | 2 |
| **B30** | 40.6 | 4.75 | 81 | 10.2 | 6.03 | 17 | -18.8 | 2.13 | 2 |

**Table S4.** Fitting parameters which describe P speciation in this series of glasses. Uncertainties in $\delta_{CS}$ and full width at half maximum (FWHM) are both on the order of $\pm\,0.5$ ppm.

| Glass ID | $\delta_{CS}$ (ppm) | FWHM (ppm) |
|----------|---------------------|------------|
| **B16** | -34.0 | 15.9 |
| **B22** | -33.6 | 15.9 |
| **B24** | -33.6 | 15.9 |
| **B26** | -33.6 | 15.9 |
| **B28** | -33.4 | 16.1 |
| **B30** | -33.6 | 15.9 |
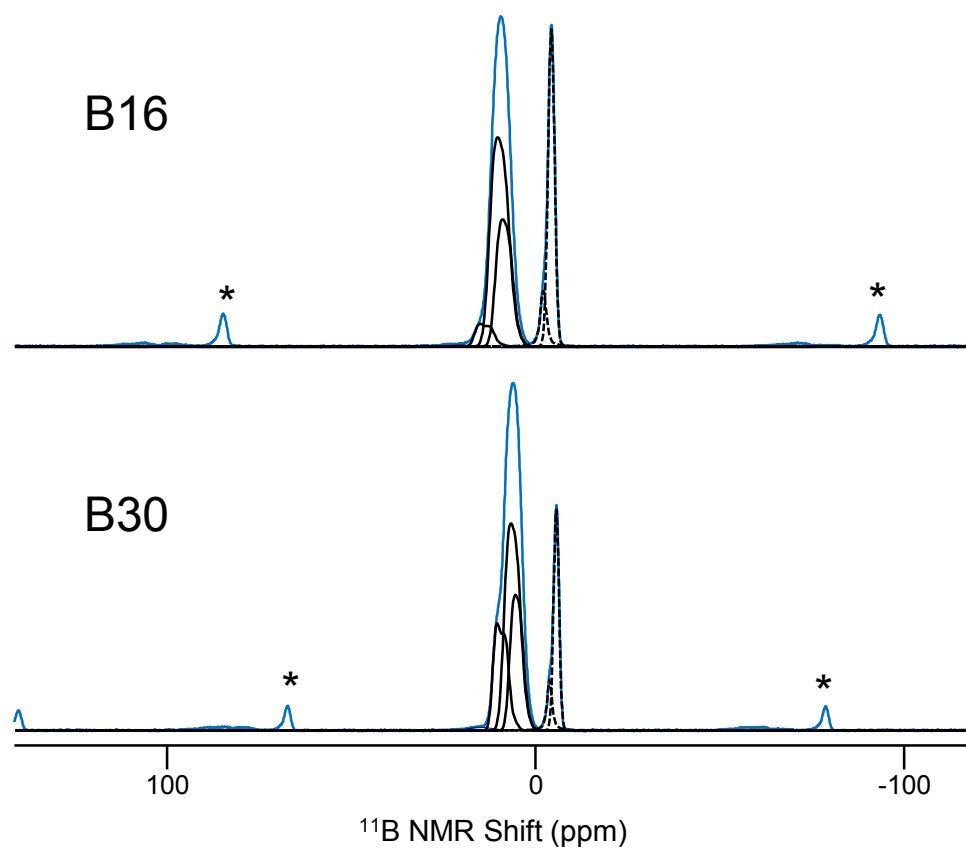
**Figure S1.** ^{11}B MAS NMR spectra of B16 and B30 glasses and their respective fits. Blue lines represent the experimental data. Dashed and solid black curves show the two $B^{IV}$ peaks and three $B^{III}$ resonances, respectively. Asterisks mark the position of sidebands, which were considered in all fits of these data.

**Figures S2.** $^{27}$Al MAS NMR spectra of B16 and B30 glasses, with fitting of resonances from Al$^{IV}$, Al$^{V}$ and Al$^{VI}$ species (shaded curves).
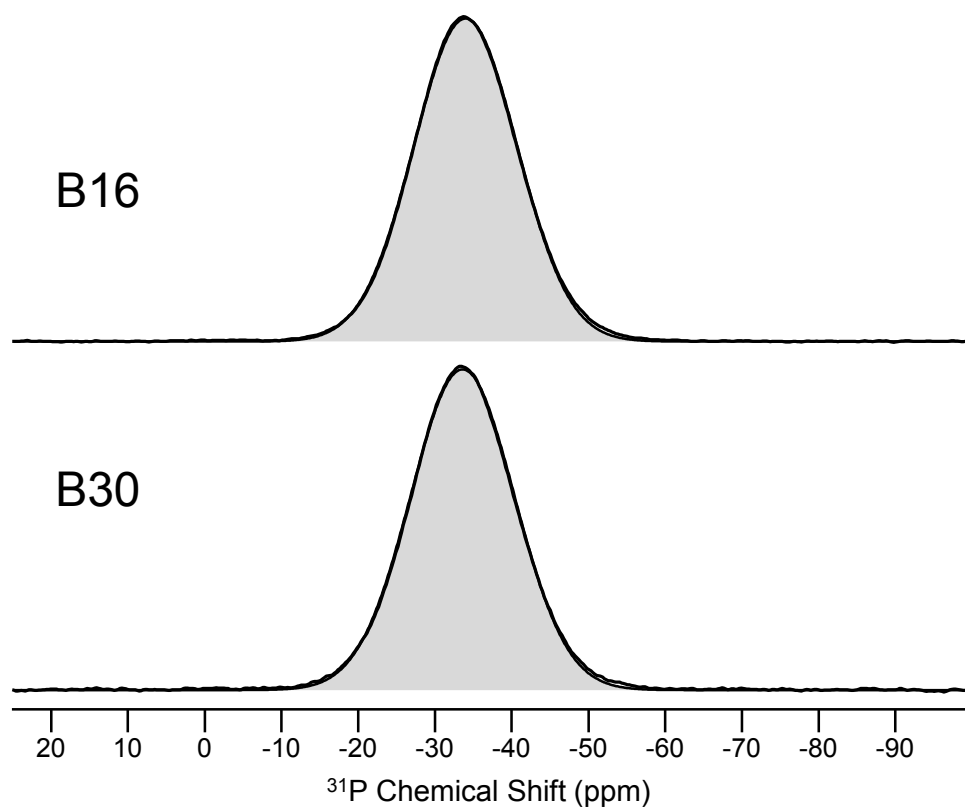
**Figure S3.** $^{31}$P MAS NMR spectra and Gaussian fits (shaded curve) for B16 and B30 glasses.